NICKEL ALUMINIDE COATING AS CATALYST IN STEAM METHANE REFORMING MICROREACTOR

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ABSTRACT

The catalyst deposition in microreactor for steam methane reforming (SMR) on a micro-scale poses new opportunities due to lack of literatures. Using plate-type catalyst as a basis, a foundation work on the preparation and analysis of catalyst deposition, specifically by dip coating (DC) method was conducted. This study which to deposit nickel aluminide catalyst on stainless steel 304 (SS304) substrate plates with different roughness and DC withdrawal speed has been conducted. Analysis of calcination temperatures on nickel aluminide thin film, followed by characterization of nickel aluminide thin film, then tested with SMR yield were performed. The studied parameters used DC withdrawals speed of 40, 80, 120, 160 and 200 mm/min. Next, calcination temperatures of 300, 400, 500 and 600°C for 90 minutes each were tested. All deposited substrates were characterized using Atomic Force Microscopy (AFM) and X-ray Diffraction (XRD). Polished substrate produced average surface roughness 0.18, 0.13 and 0.09 µm. The Atomic Force Microscopy results showed that film thickness and roughness are proportional to the withdrawal speed, however, the inverse effect on sol-gel adhesion on the substrate due to gravitational drag force limitation. Substrate with roughness of 0.13 µm and dip coating withdrawal speed 160mm/min shows the highest coating thickness and surface roughness. The nickel aluminide catalyst film‘s average roughness (R_a) and ten-point mean height (R_z) had increased proportionally when the calcination temperature increases from 300 to 500°C, but not at 600°C. In addition, higher calcination temperature produces more Nickel aluminide compared to lower calcination temperature. The deposited catalyst was activated using hydrogen and then tested in an SMR microreactor. Results showed that using this catalyst, a mixture of steam and methane were reformed to hydrogen and carbon monoxide at temperature between 550°C and 650°C. Thus, it is confirmed that the method applied in this study was able to produce a functioning nickel aluminide catalyst for SMR microreactor.

ABSTRAK

Pendepositan pemangkin di dalam reaktor mikro untuk pembaharuan stim metana (SMR) pada sekala mikro wujud pelbagai peluang baharu dengan menggunakan pemangkin jenis plat. Kajian asas dan analisis untuk penyedian pemendapan pemangkin menggunakan kaedah celupan (DC) telah dijalankan. Kajian ini bertujuan untuk mendepositkan pemangkin nikel aluminida pada plat tahan karat (SS304) dengan kekasaran dan kelajuan pengeluaran celupan DC yang berbeza telah dijalankan. Analisis dan pencirian kesan suhu kalsinasi pada filem nikel aluminida telah dilakukan, seterusnya diuji di dalam reaktor mikro. Parameter yang dikaji menggunakan kelajuan pengeluaran celupan 40, 80, 120, 160 dan 200 mm / min. Seterusnya, suhu kalcinasi pada 300, 400, 500 dan 600 °C selama 90 minit telah diuji. Semua substrat yang telah disalut telah dicirikan menggunakan Atomic Force Microscopy (AFM) dan X-ray Diffraction (XRD). Substrat yang telah digilap menggunakan kertas pasir menghasilkan permukaan kekasaran 0.18, 0.13 dan 0.09 μm. Hasil pemerhatian AFM menunjukkan bahawa kesan songsang pada lekatan sol-gel pada substrat disebabkan oleh batasan kuasa drag graviti. Kekasaran substrat pada 0.13 μm dan kadar pengeluaran celupan pada 160mm/min menghasilkan ketebalan lapisan tertinggi dan permukaan terkasar. Purata kekasaran (R_a) filem pemangkin nikel aluminida dan ketinggian sepuluh titik ketinggian (R_z) meningkat secara beransur-ansur apabila suhu kalsinasi meningkat daripada 300°C kepada 500°C, tetapi tidak pada 600°C. Di samping itu, dengan suhu kalsinasi yang lebih tinggi menghasilkan lebih banyak nikel aluminida berbanding suhu kalsinasi yang lebih rendah. Keputusan menunjukkan bahawa dengan menggunakan pemangkin ini, campuran stim dan metana telah berjaya dipecah kepada hidrogen dan karbon monoksida pada suhu antara 550°C dan 650°C. Ia mengesahkan bahawa kaedah yang digunakan dalam kajian ini berjaya menghasilkan pemangkin nikel aluminida yang berfungsi untuk reaktor mikro SMR.

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LIST OF SYMBOLS AND ABBREVIATIONS

AFM	-	Atomic Force Microscope
Al	-	Aluminum
Al_2O_3	-	Alumina
Au	-	Gold
CH_4	-	Methane
CNG	-	Compressed Natural Gas
CO	-	Carbon Monoxide
CO_2	-	Carbon Dioxide
CVD	-	Chemical Vapor Deposition
Cr	-	Chromium
EDS	-	Energy Dispersive Spectroscopy
FSD	-	Flame Spray Deposition
GC	-	Gas Chromatography
h	-	Coating thickness (μm)
H_2	-	Hydrogen
H_2O	-	Water / Steam
Hz	-	Hertz
Ir	-	Iridium
K	-	Potassium
L	-	Liter
min	-	minute
mm/min	-	millimeter per minute
Ni/Al_2O_3	-	Nickel Alumina
Ni	-	Nickel
Ni_3Al	-	Nickel Aluminide

NiAl	-	Nickel Aluminide
Ni-Al	-	Nickel Aluminum
nm	-	nanometer
O_2	-	Oxygen
P	-	Pressure (Bar)
Pd	-	Palladium
Pt	-	Platinum
R_a	-	Average roughness (µm)
R_z	-	Roughness ten-point mean height
R_q	-	Roughness root mean squared
R_{sk}	-	Roughness skewness
R_{ku}	-	Roughness kurtosis
Rh	-	Rhodium
Ru	-	Ruthenium
SEM	-	Scanning Electron Microscopy
Syngas	-	Synthesis Gas
SS304	-	Stainless Steel 304
S/C	-	Steam to carbon ratio
Sol-gel	-	Solution gelatin
SMR	-	Steam Methane Reforming
T	-	Temperature (°C)
t	-	time (min)
TCD	-	Temperature Control Detector
XRD	-	X-ray Diffraction
Zn	-	Zinc
v	-	Withdrawal speed (mm/min)
wt%	-	Weighted percent
%	-	Percentage
°C	-	Degree Celsius
µm	-	micrometer

CHAPTER 1

INTRODUCTION

1.1 Research Background

Currently, the world's energy demand had grown nearly one-third between 2013 and 2040 [1]. Proportionally increased in energy demand also increased the greenhouse-gas (GHG) emissions. The energy sector must be at the heart of global action to deal with climate change. According to World Energy Outlook 2015 Factsheet in a climate meeting in Paris on December 2015 over 150 countries have submitted pledges to reduce emissions. Around half of these submissions include explicit energy-focused targets, either alongside a GHG emissions target or as a stand-alone goal. The most common energy-related measures are those that targeted an increase in renewables deployment (40% of submissions) or in improvement energy efficiency (one-third of submissions) [1]. In order to reduce the shared emission problem, many steps had been taken and one of them is by using hydrogen as fuel.

The production of hydrogen from various hydrocarbons especially methane mainly comes from the chemical reaction process of catalytic reforming technologies, which consist of steam reforming, partial oxidation, and auto thermal reforming. Catalytic SMR has the advantage of relatively low reaction temperature and high hydrogen content in the reforming products as shown in Table 1.1. Currently SMR is regarded as the most cost effective and highly developed type of reforming for large scale hydrogen production [2][3].

Table 1.1 : Hydrogen production technologies summary [2]

Technology	Feedstock	Efficiency	Maturity
Steam reforming	Hydrocarbons	70-85%	Commercial
Partial oxidation	Hydrocarbons	60-75%	Commercial
Autothermal reforming	Hydrocarbons	60-75%	Near term
Plasma reforming	Hydrocarbons	9-85%	Long term
Biomass gasification	Biomass	35-50%	Commercial
Aqueous phase reforming	Carbohydrates	35-55%	Med. term
Electrolysis	H_2O + electricity	50-70%	Commercial
Photolysis	H_2O + sunlight	0.5%	Long term
Thermochemical water splitting	H_2O + heat	NA	Long term

Currently, the synthesis gas (syngas) from the SMR, which is the mixture of hydrogen and carbon monoxide, had become important feedstock to chemical industry with large-scale production. It is mainly produced by steam reforming of Compressed Natural Gas (CNG), composed mostly of methane and in tubular reactors packed with Ni-based catalysts. The SMR of natural gas is the main commercial process for synthesis gas production (H_2, CO and very often CO_2). In this process, methane reacts with steam to produce a mixture of hydrogen, carbon monoxide. This reaction is highly endothermic and is performed in the presence of a catalyst such as Ni or noble metal at high temperature (700–1000 °C) [4] . The reaction requires the external heating of the reactor tubes which is carried out either by direct firing (as in radiant reformers) or by heat exchange with a hot stream (as in convective reformers) [5].

It is widely accepted that hydrogen is among the clean, efficient and pollution free energy source in the future. Hydrogen is a potential source of clean energy mainly as fuel in fuel-cell systems, which described as continuously operating batteries[6]. Hydrogen is widely used feedstock in the chemical, food, and refining industries. The demand for hydrogen is expected to drastically increase, because of its potential as a major energy source in the future [5]. The use of hydrogen for petrochemicals, fertilizers and as energy carrier in connection with renewable energy production will increase substantially in the next 5 to 10 years. Low sulfur gasoline and diesel fuels will become mandatory and harmful emissions will be reduced drastically. Hydrogen will be required by refiners and specialty chemical manufacturers to meet the global need for cleaner products.

The growing fuel cell market will be dependent on hydrogen as a primary fuel source [7]. Moreover, lots of attention had been paid to hydrogen production technology in order to obtain a stable source of hydrogen. Currently, almost 96% of the world's hydrogen demand is supplied by traditional fossil fuels as shown in Figure 1.1, and about half of it is comes from natural gas which the main composition is methane [8].

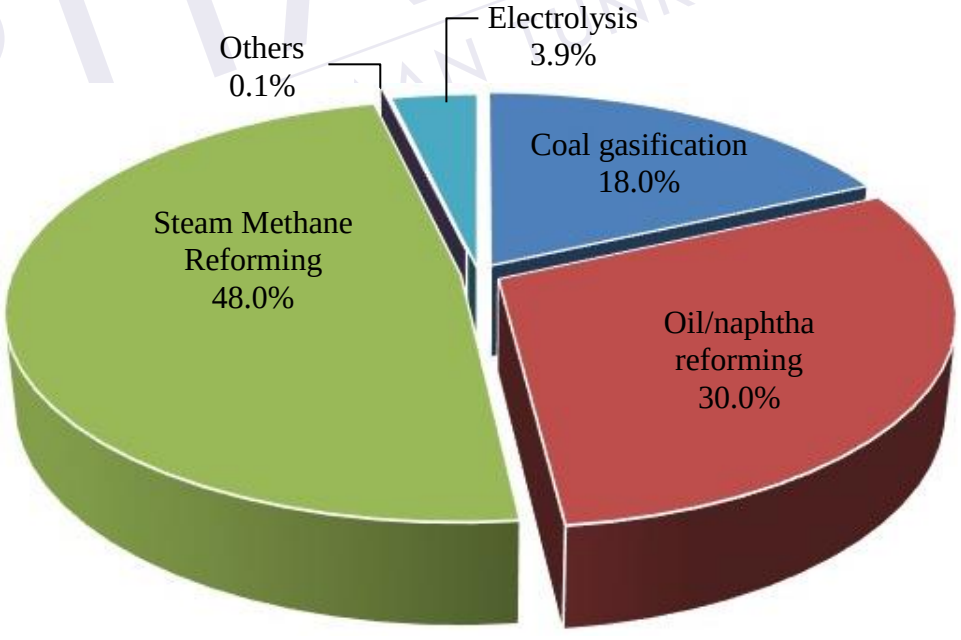

Figure 1.1: Distribution of primary energy sources for hydrogen production [8][9]

The SMR is regarded as the most economical method for producing hydrogen and is the most widely used. Normal operating SMR required the aids of the catalyst deposited in a reactor to reduce the catalytic energy required for conversion. By definition, microreactor technology is a reduction in size of chemical reactor into sub-micron or sub-millimeter which roughly around 50μm to 2mm [10]. The SMR microreactor has the advantage of high surface to volume ratio, high heat and mass transfer rate. Furthermore, the SMR microreactors are safe to operate, have low operation, maintenance and construction costs, short residence times, high energy efficiency and materials efficiency [10][11][12]. There are a few type of microreactor and design depending on the industrial application. Although the design of the microreactor was varied, their purpose is the same which is to carry out catalytic conversion with a catalyst assistant. Basically, the design of the microreactor comprise of microchannels inlet and outlet as shown in Figure 1.2.

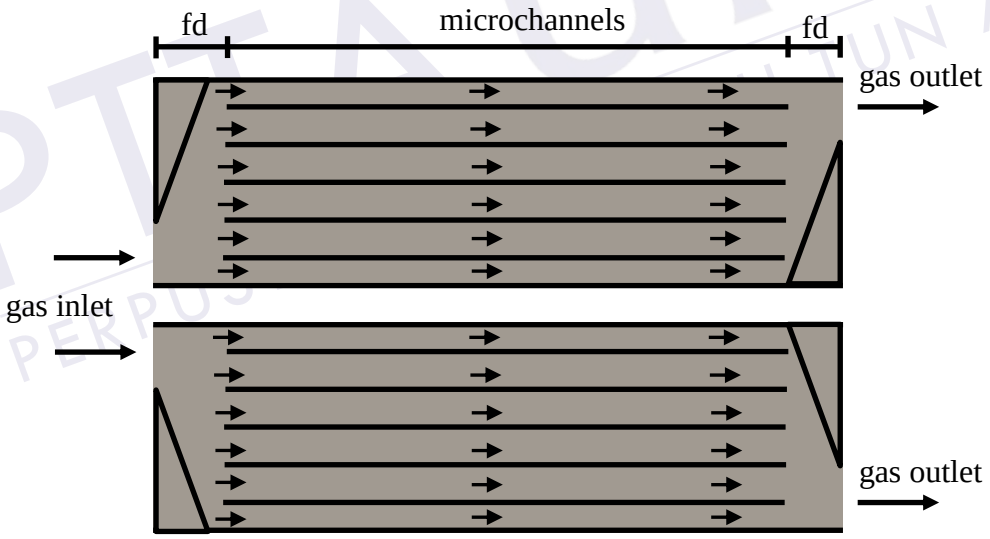

Figure 1.2: Schematic drawing of the microstructure plates. Plates contain flow distribution chambers (fd) and microchannels. Alternating stacking of the mirror images of the microstructure plates creates a heat exchanger [11]

Many researcher had studied and established the formulation method for SMR catalyst. They can be divided into three general classification, bulk catalyst, impregnated catalyst and physical mixing catalysts [13]. Under the bulk catalyst there are two categories which are precipitation process and sol-gel process. The Precipitation process is not very inconvenient since its required high temperature. The sol-gel method is a chemical synthesis technique which often implies some jellification steps. Common ingredient for this method are catalyst support or catalyst itself, binder, acid and water. The concentration of the ingredient can be varied based on the desired coating characteristic. The impregnation method employ impregnated catalyst through bulk preparation and catalytic active metals. A lot of hydrogenation catalysts were prepared through this way. On the other hand, physical mixing method is prepared by physically mixing the catalyst with a powder support in ball mill. There were also a lot of catalyst deposition method which can be employed for preparing the catalyst such as dip coating, spin coating, spray coating, chemical vapor deposition (CVD) and flame spray deposition (FSD) [14].

Among the technique listed, dip coating is the most simplest and has great potential to be studied. Dip coating has the ability to provide easier and economical way to deposit thin film of solutions onto a plate or micro structured plate [15][16]. This method enables the formation of highly ordered film with favorable surface properties [17]. The thickness of film can be tailored by controlling the withdrawal speed of the substrate [16][18]. The solutions can be prepared by sol-gel route to obtain homogeneous Ni catalyst solutions. A sol-gel of Ni based catalyst can be employed as thin layer (<100μm) on the substrate plate to reduce mass and heat transfer limitations compared with pellet catalyst [19].

1.1.1 Nickel Aluminide Catalyst Preparation Overview

Intermetallic compounds are scarcely investigated especially for catalysis [20]. The difficulty concerning their synthesis and their structural complexity are the main reason its lack of study. nickel aluminide such as Ni_3Al and NiAl have the potential for catalysis because of it good selectivity and activity [21]. Commonly, nickel aluminide catalyst were prepared through chemical leaching or catalyst impregnation and was proven in the methanol decomposition and SMR. The preparation through sol-gel and dip coating has the potential to be investigated since it is cheap and easy to control.

In catalyst preparation through dip coating technique, there are a few parameter which required attention as shown in Figure 1.3. First of all is the materials used as the substrate, which must be to withstand high temperature for SMR operation. Furthermore, for coating process the surface of the substrate must be clean and possess the ability for catalyst solution adhesion. For the solution preparation, parameters that should be focused are catalyst weight percent, solution‘s pH value, aging time and also support materials, all of which would affect the selectivity and reactivity of the catalsyt.

The dip coating process can be controlled through many parameters such as dipping speed, withdrawal speed, dipping time, dipping cycles, drying time and temperature between cycles. Among the parameter mentioned, previous researcher had studied the effect of withdrawal speed, dipping speed, dipping cycles and drying temperature between cycles[15][18]. The parameter studied affect the thickness, roughness and surface area of the catalyst coated.

The last step involved in the catalyst preparation is calcination process. During calcination, the temperature and its duration can affect the topography and morphology of the film produced on the substrate. Controlling the temperature and duration would be able to produce desired coating characteristics.

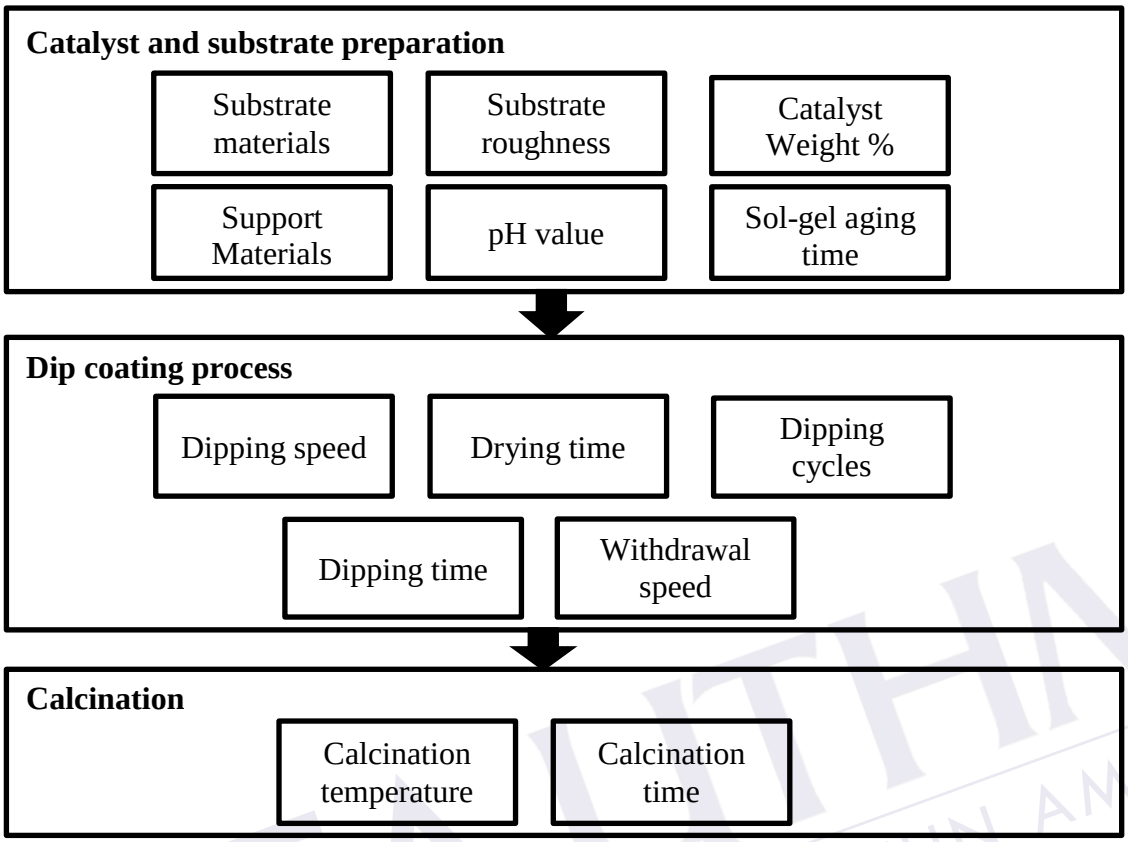

Figure 1.3: Factors affecting catalyst deposition using DC method as summarized from [22][23][24][25][26][27]

1.2 Problem Statement

Coating nickel aluminide on metallic substrate using DC method is challenging because of the coating adhesion limitation and lack in roughness quantifying. The adhesion between coated film and substrate can be improve through surface treatment which also would increase the substrate surface roughness. The pre-treatment of the substrate to coat is gaining more and more importance because it allows to increase the adherence of the catalytic layer and thus the life time of the structured catalyst [28]. The most important characteristics of the catalyst are the high surface roughness which contribute to the whole total surface area and the well distribution or dispersion of catalyst on the surface [29]. High surface area can facilitate the dispersion of Ni and create more active sites with small particle size from the porous structure [30].

Furthermore, during the dip coating process, the thickness and roughness were influenced by the withdrawal speed of the substrate [15]. Moreover, with the aid of sol-gel preparation, it enable precise controlled and tuning of the catalyst microstructure [14]. Currently there is still unknown withdrawal speed for DC method specifically through sol-gel preparation. Further study is required to determine the most optimum withdrawal speed for nickel aluminide catalyst deposition.

The formation of the nickel aluminide intermetallic compounds were affected by the treatment temperature. Furthermore, the calcination temperature is varied for different catalyst to allowed the formation of nickel aluminide compounds [31]. Therefore, this fundamental studies are required for preparing SMR catalyst especially using nickel aluminide compounds.

Calcined samples need to be activated in the flow of H_2 through reduction process. Different compound had different reduction temperature. It is also important to determine the right activation temperature to ensure the best catalyst performance. The catalyst testing is required to determine its usability in microreactor for SMR.

1.3 Objectives

The objectives of this research are as follows:

i. To deposit nickel aluminide on SS304 substrate using the dip coating method
ii. To investigate SS304 substrate roughness effect on nickel aluminide catalyst coating
iii. To evaluate the effect of substrate withdrawal speed on nickel aluminide film thickness and roughness
iv. To investigate the calcination temperature effect on nickel aluminide catalyst coating characteristics
v. To verify that the coated and activated nickel aluminide catalyst capability in producing syngas in a SMR microreactor.

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